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Mössbauer spectroscopy : an excellent technique to characterize magnetic materials of nanometer dimension

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Abstract Effectiveness of Mössbauer spectroscopy in characterizing nanometric magnetic materials are highlighted with the spectra recorded at different temperatures for nanocrystalline cobalt ferrite, α- Fe_2O_3 and nanocomposites of Fe-SiO_2 and Fe-Fe_3O_4. It is shown that in superparamagnetic state when the effective internal magnetic field at the probe nucleus is zero resulting in the collapse of the sextet pattern, the quadrupolar interaction can be used to identify the nanoparticles.

Keywords Mössbauer spectroscopy, superparamagnetism, nanocrystallites

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1. Introduction

Mössbauer spectroscopy has become an essential tool to characterize magnetic materials of nanometer dimension because of its ability to probe microscopically the immediate environment of the nucleus through hyperfine interaction namely the interaction between the nuclear charge and the electromagnetic field generated by the extra-nuclear electrons. In the bulk or crystalline state, ferromagnetic, ferrimagnetic or anti-ferromagnetic classes of materials produce large internal magnetic field at the nucleus. This internal field is mainly created by the net *s*-electron spin density giving rise to splitting of the nuclear energy levels and a characteristic six-finger Mössbauer spectrum. In the nanocrystalline state, if the magnetic anisotropy energy of a crystallite which is proportional to the volume of the crystallite becomes smaller than the Boltzman's thermal energy (k_BT) at a particular temperature, the net magnetic moment of the crystallite relaxes between the easy axes of magnetization leading to superparamagnetism. If the frequency of such relaxation is faster than the Larmor precession frequency of the nucleus (~10^{-8} sec), the average magnetic field at the nucleus becomes zero and the six-finger Mössbauer pattern collapses to a doublet or singlet depending on whether the electric field gradient at the nucleus is present or absent respectively. Thus, Mössbauer technique determines in a simple and straightforward way the presence of nano-particles undergoing superparamagnetic (SPM) relaxation in magnetic materials.

In the present paper the effectiveness of the Mössbauer spectroscopy in characterizing the magnetic nanoparticles are highlighted by taking specific examples of nanoparticles of cobalt ferrite and alpha ferric oxide as well as nanocomposites of Fe-SiO_2 and Fe-Fe_3O_4.

2. Superparamagnetism and Mössbauer spectroscopy

Nanocrystalline magnetic particles are often single domain particles. The magnetic energy of such particles with uniaxial anisotropy is given by

$$E = KV \sin^2 \theta$$

where K = anisotropy constant, V = volume and θ is the angle between the magnetization direction and easy axis of magnetization.

For extremely small particles, the energy barrier KV which separates the two energy minima at $\theta = 0°$ and $\theta = 180°$, may be smaller than the thermal energy (k_BT) even at room temperature. This leads to the spontaneous fluctuation of the magnetization direction known as superparamagnetic relaxation with frequency given by

$$\tau = \tau_0 \exp(KV / k_BT)$$

where τ_0 is the natural frequency of gyromagnetic precession and is of the order of 10^{-10}–10^{-13} s and k_B is Boltzman's constant.

Superparamagnetic behavior may be observed using a technique with characteristic time (τ_m), at temperatures above the so called blocking temperature (T_B), defined as

$$T_B = KV / k_B \ln(\tau_m/\tau_0)$$

Above the blocking temperature, the relaxation frequency $\tau >> \tau_m$ ($\sim 10^{-8}$ s for ^{57}Fe Mössbauer spectroscopy) and the internal magnetic field at the nucleus is averaged out giving rise to usually a doublet Mossbauer pattern.

Below the blocking temperature, $\tau << \tau_m$ and a characteristic Mössbauer sextet pattern is ovserved.

When, $\tau \approx \tau_m$ a partially collapsed sextet is observed.

3. Nanocrystalline cobalt ferrite

Nanocrystalline cobalt ferrite samples with average size ranging from 6 nm to 20 nm had been prepared at room temperature by a chemical route and characterized by Mössbauer spectroscopy [1]. Mössbauer spectra recorded at room temperature of the samples with different crystallite sizes are shown in Figure 1. As seen from Figure 1, the 6 nm sized sample gives a strong quadrupole doublet with a weak partially collapsed sextet. The doublet is assigned to ultrafine particles undergoing superparamagnetic relaxation for which the relaxation frequency at room temperature τ is much larger than τ_m. The partially collapsed sextet is due to larger crystallites in the sample with $\tau \sim \tau_m$. Another point to be noted is the large quadrupole splitting (QS) 0.76 mm/s of the doublet. In the bulk form, cobalt ferrite being a cubic spinel [2] gives negligibly small QS for Fe atoms in tetrahedral (A) sites and QS of the order of 0.40 mm/s for Fe atoms in octahedral (B) sites. In nanocrystalline state, number of atoms in the grain boundaries becomes significant because of the large surface to volume ratio. These atoms experience large electric field gradient (EFG) due to surface irregularities giving rise to large quadrupole splitting. For 12 nm sized particle the sextet pattern becomes prominent at the cost of the doublet because the number of large crystallites in the sample is expected to be more with the increase of average crystallite size. Spectrum of 30 nm sized particle shows a well defined sextet indicating that all the atoms experience static hyperfine field characteristic of a magnetically ordered state

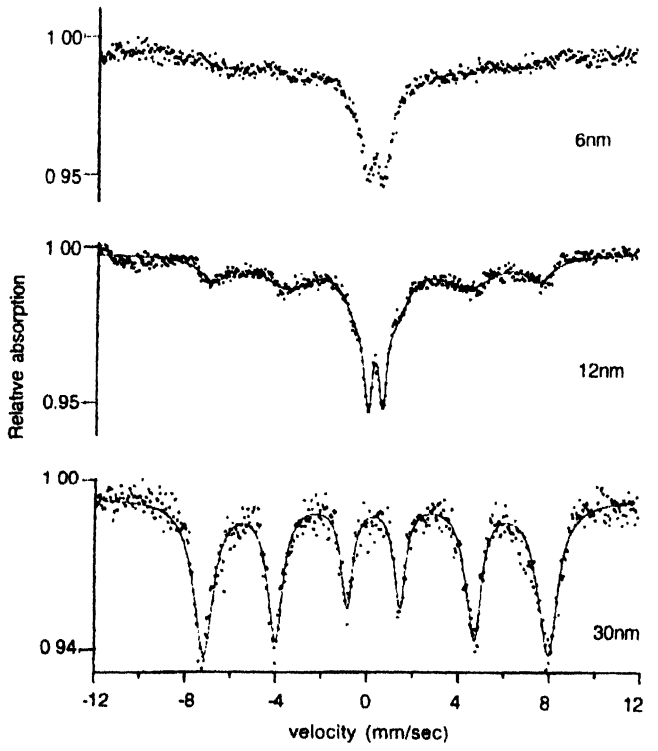

Figure 1. Mössbauer spectra at room temperature of $CoFe_2O_4$ samples with size 6 nm, 12 nm and 30 nm.

Figure 2 shows spectra of 6 nm particles as a function of temperature. At 150 K, the doublet seen at room temperature disappears showing a sextet pattern which becomes sharp and well define as the temperature is lowered to 40 K. With lowering of temperature the superparamagnetic relaxation frequency τ of nanocrystallites becomes slower and at temperatures when it becomes far less than τ_m a sextet pattern evolves.

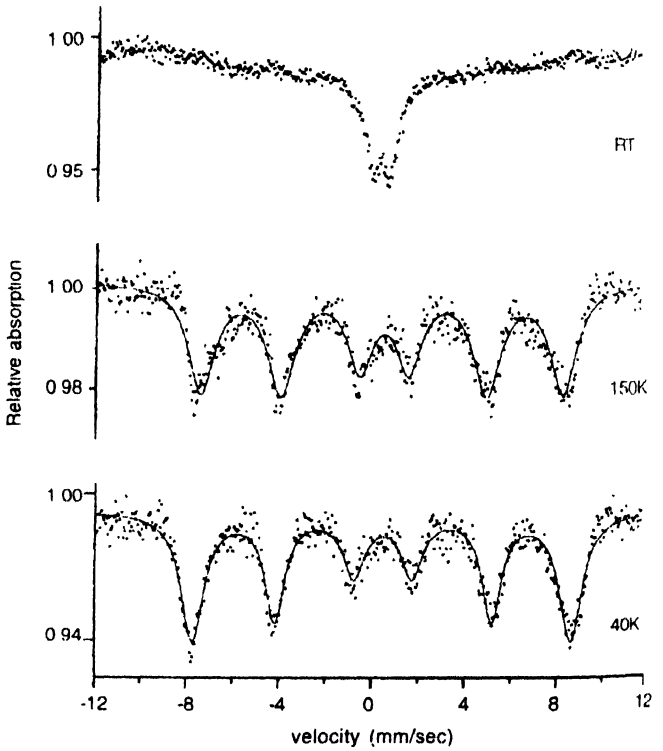

Figure 2. Mössbauer spectra of 6nm $CoFe_2O_4$ sample at different temperatures.

4. Nanocrystalline α-Fe_2O_3

Nanocrystalline α-Fe_2O_3 with crystallite size ranging from 17 nm to 55 nm have been prepared using a sol-gel route [3] Mössbauer spectra recorded at room temperature of the samples with different sizes are shown in Figure 3. Spectrum of the sample with an average size of 17 nm shows a broad asymmetric sextet superposed on a doublet. The spectrum was fitted with

three symmetric sextets and a doublet. The sharp sextet with fractional area 19% and isomer shift (IS) 0.52 mm/s, quadrupole splitting (QS) 0.20 mm/s and internal field (H_{int}) 513 kOe is attributed to crystalline component present in the sample. The second sextet with 14% fractional area and larger QS (0.45 mm/s) and reduced H_{int} (492 kOe) in comparison with that of crystalline component is attributed to finer particles within the nanocrystallites experiencing enhanced EFG due to lattice strain [4]. The third sextet (fractional area 49%) with very broad lines and larger QS (0.62 mm/s) and very much reduced H_{int} (447 kOe) compared with that of crystalline part is attributed to the interfacial atoms situated on the grain boundaries. The central doublet with fractional area of 18% is assigned to single domain nanocrystals undergoing SPM relaxation. With the increase of particle size up to 22 nm the intensity of the crystalline part was found to increase at the cost of the interfacial and SPM fractions which clearly indicates the grain growth resulting in formation of crystallites of larger average size. Beyond 30 nm a magnetically ordered sextet is observed with no signature of SPM fraction.

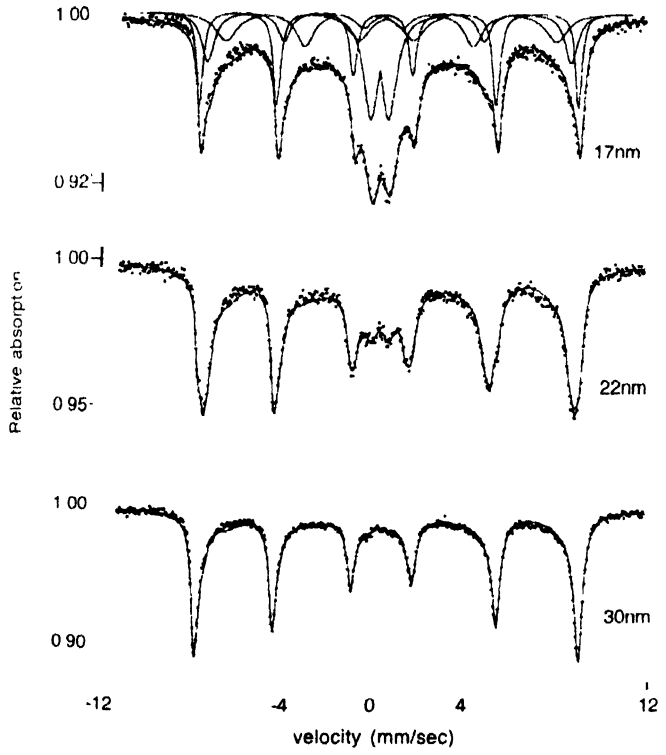

Figure 3. Mössbauer spectra at room temperature of α-Fe_2O_3 particles of different size.

5. Nanocomposites of Fe-SiO_2

Nanocomposites of Fe-SiO_2 with average size varying from 1.8 nm to 9.5 nm were characterized by Mössbauer spectroscopy [5]. The samples were prepared by a sol-gel technique. Figure 4 shows Mössbauer spectra of the sample with average size 1.8 nm. A strong central doublet superposed on a distinct sextet is seen at room temperature. The sextet with hyperfine field 337 kOe was attributed to Fe particles for which the blocking temperature is above the room temperature. The slight enhancement of the H_{int} compared with the bulk value (330 kOe) is signature of the ultrafine nature of the sample as has been reported by others [6]. The central doublet is assigned to particles undergoing SPM relaxation. The large QS (0.69 mm/s) of the doublet indicates loss of cubic symmetry at the Fe site because of surface effects [7]. At 115 K , the intensity of the sextet was found to increase at the cost of the doublet which confirms the assignment of the doublet to SPM relaxation.

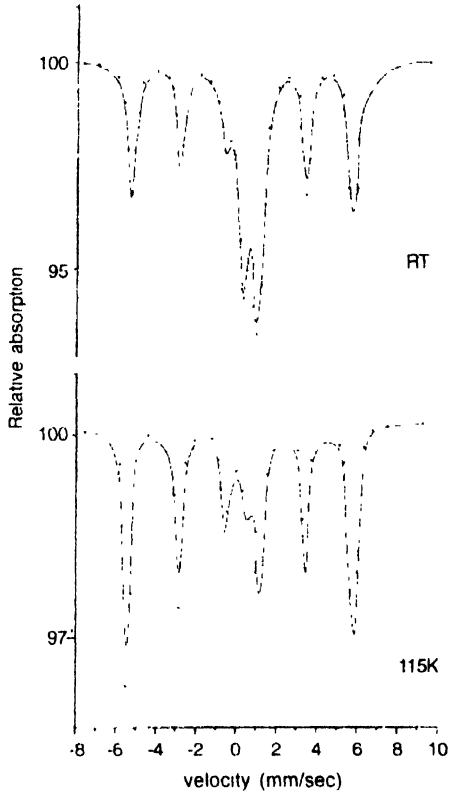

Figure 4. Mössbauer spectra of 1.8 nm Fe-SiO_2 nanocomposite

For 3.7 nm and 9.5 nm sized particles similar Mössbauer pattern as shown in Figure 4 were observed with gradual reduction of intensity of SPM fraction as expected.

6. Nanocomposites of Fe-Fe_3O_4

Nanocomposites of Fe-Fe_3O_4 having dimension in the range 10–20 nm were prepared by a simple reduction method starting with micrometer sized alpha ferric oxide [8]. Figure 5 shows a typical spectrum recorded for particles with average size of 17 nm. As can be seen from the figure the spectrum could be fitted with three sextets and a doublet. The sharp sextet with almost zero isomer shift and H_{int} 330 kOe has been identified as due to alpha iron. The sextets with H_{int} 495 kOe and 463 kOe have been assigned to A site and B site of Fe_3O_4 respectively. These are due to larger crystallites in the sample with blocking temperature above the room temperature. The doublet is due to SPM particles

of alpha Fe and/or Fe_3O_4. At 70 K the doublet almost disappeared confirming its assignment as due to SPM particles.

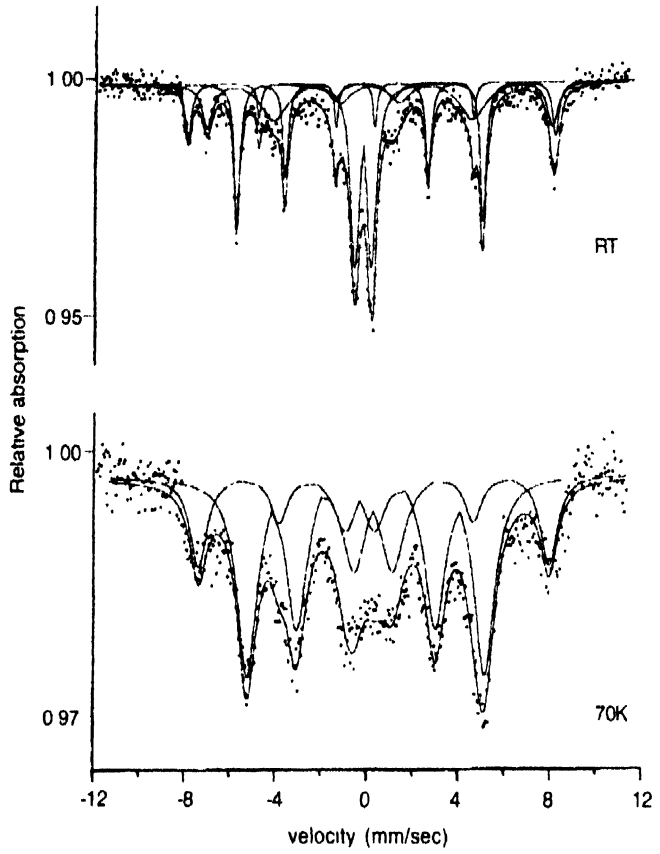

Figure 5. Mössbuer spectra of 17 nm Fe-Fe_3O_4 nanocomposite

7. Conclusion

From the examples as given above it is clear that Mössbauer spectroscopy can be effectively applied to characterize nanometric magnetic particles. The Mössbauer spectra recorded at various temperatures can be used to confirm the existence of nanocrystallites in a sample. In the superparamagnetic state the quadrupole splitting gives information about the atoms located near the grain boundaries.

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